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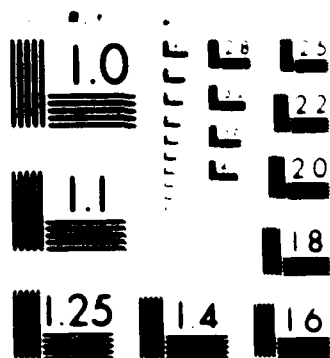
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Hydrazine Complexes of *B*-Triorganylborrowins¹

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Received.....

Abstract

B-Triorganylborrowins, $(-BRO-)_3$ ($R = C_2H_5, C_6H_5$), form 1:1 molar complexes with hydrazine, *N,N'*-dimethylhydrazine, and *N,N*-dimethylhydrazine. At room temperature, the complexes exhibit only one ¹¹B NMR signal suggesting that the species are fluxional with nitrogen coordinating to all three boron atoms of the boroxin ring. The signals broaden on lowering of the temperature and, at -50 °C, the signal of $(-BC_2H_5O-)_3 \cdot (CH_3)_2NNH_2$ appears as two separate peaks in 2:1 ratio indicating that fluxion has been arrested. The complexes $(-BRO-)_3 \cdot L$ with $R = C_2H_5$ or C_6H_5 and $L = N_2H_4$ and with $R = C_6H_5$ and $L = (CH_3)_2NNH_2$ can form solvates with excess of the hydrazine and solid 1:2 molar complexes were isolated. However, the second hydrazine is readily lost under reduced pressure or at elevated temperatures. The complexes of *B*-triphenylboroxin are thermally much less stable than those of *B*-triethylboroxin.

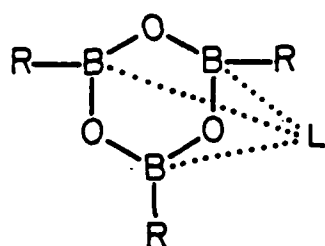
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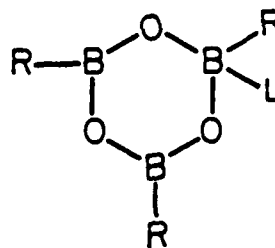
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Introduction

It has been known for a long time that *B*-triorganylborexins, $(-\text{BRO}-)_3$, form 1:1 molar adducts with amines ($=\text{L}$) to yield species of the type $(-\text{BRO}-)_3\cdot\text{L}$.² The structures of such complexes have been studied only recently. Fluxional attachment of L to all three boron atoms of the boroxin as shown in A (below) was indicated by a single ^{11}B NMR signal, said to persist even at low temperatures.³ In more recent work, however, it was shown that at -20°C the ^{11}B NMR signal of $(-\text{BC}_2\text{H}_5\text{O}-)_3\cdot\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$ (which is at 23.8 ppm at ambient temperature) is split in two signals at 30.9 and 5.7 ppm, respectively, and in an area ratio of 2:1. This illustrates that at low temperatures the amine is coordinated to a single boron atom of the boroxin ring, leaving the other two boron atoms in an sp^2 environment (B, below). Indeed, low temperature ^1H NMR spectra of several adducts of the type $(-\text{BC}_6\text{H}_5\text{O}-)_3\cdot\text{L}$ exhibited similar signal splitting, thus substantiating a slowing down of the fluxionality with a lowering of the temperature.⁴



A



B

In this context it is worth noting that *p*-phenylenediamine forms a 3:2 molar complex with *B*-triphenylboroxin.⁵ However, crystal structure data show that only one of the three diamine molecules is directly involved in the bonding and donates each of its two nitrogen atoms to a boron atom of a different boroxin ring. The remaining two amine molecules merely fill the empty space in the lattice structure.⁴ This situation is similar to that encountered for the 1:2 molar adduct of 1,4-diazabicyclo[2.2.2]octane with *B*-triphenylboroxin. Here again each nitrogen atom of the base donates to one boron atom of a different boroxin ring and the crystal structure is stabilized by three solvent (benzene) molecules.⁴

B-Triorganylborexins also form 1:1 molar adducts with pyrazole and C-substituted derivatives thereof. However, in this case the two donor sites of the pyrazole molecule both seem to interact with boron atoms of the same boroxin ring. Moreover, subsequent interaction of such adducts with additional pyrazole can lead to a condensation reaction and thereby to the formation of unusual triply bridged pyrazabole structures by amination of boron-oxygen bonds, even at room temperature.⁶

In order to obtain a better understanding of the interaction of nitrogen donor molecules with *B*-triorganylborexins, reactions of the latter with hydrazines have been investigated.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded of solutions in CDCl_3 on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal Me_4Si for ^1H NMR, external $\text{Et}_2\text{O}\cdot\text{BF}_3$ for ^{11}B NMR); s = singlet, t = triplet, q = quartet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in Hz. Mass spectral data were recorded on a VG ZAB-2F spectrometer, infrared data were obtained on a PE Model 621 instrument.

$(-\text{BC}_2\text{H}_5\text{O})_3\cdot(\text{CH}_3)_2\text{NNH}_2$. Under inert atmosphere, 2.3 g (38 mmol) of anhydrous *N,N*-dimethylhydrazine was added dropwise and with stirring to 6.0 g (36 mmol) of *B*-triethylboroxin. An exothermic reaction occurred and the mixture was allowed to cool to room temperature with stirring. Subsequent distillation under vacuum gave 7.0 g (86%) of the desired compound, bp $61^\circ\text{C}/2$ torr. Anal. Calcd for $\text{C}_8\text{H}_{23}\text{B}_3\text{N}_2\text{O}_3$ (M_r 227.72): C, 42.20; H, 10.18; B, 14.24; N, 12.30; O, 21.08. Found: C, 42.07; H, 10.33; B, 14.09; N, 12.04.

NMR data: $\delta(^1\text{H})$ 3.72* (2 H, s), 2.63 (6 H, s), 0.88 (9 H, t, $J = 7.5$), 0.62 (6 H, q, $J = 7.5$); $\delta(^{11}\text{B})$ 23.8 (s, $h_{1/2} = 200$ Hz). At -50°C : $\delta(^{11}\text{B})$ 31.4 (ca. 2 B), 6.9 (ca. 1 B).

$(-\text{BC}_2\text{H}_5\text{O})_3\cdot\text{CH}_3\text{HNNHCH}_3$. A solution of 4.5 g (75 mmol) of *N,N'*-dimethylhydrazine in 50 mL of ether was slowly added with stirring to a solution of 6.3 g (38 mmol) of *B*-triethylboroxin in 25 mL of ether. After subsiding of the exothermic reaction, the mixture was stirred at room temperature for 2 h and volatiles were then

removed under reduced pressure to leave 8.45 g (99%) of colorless residue. After drying under vacuum over P_4O_{10} for 24 h the material had a mp 44–46 °C (mp 45–46 °C after sublimation under vacuum at 60–80 °C bath temperature). Anal. Calcd for $C_8H_{23}B_3N_2O_3$ (M_r 227.72): C, 42.20; H, 10.18; B, 14.24; N, 12.30; O, 21.08. Found: C, 41.95; H, 10.49; B, 13.98; N, 12.19.

NMR data: $\delta(^1H)$ 4.24* (2 H, s), 2.67 (6 H, s), 0.87 (9 H, t, $J = 7.5$), 0.59 (6 H, q, $J = 7.5$); $\delta(^{11}B)$ 23.2 (s, $h_{1/2} = 280$ Hz).

$(-BC_2H_5O-)_3 \cdot N_2H_4$ was prepared in similar fashion as the preceding compound from 0.6 g (18.75 mmol) of anhydrous hydrazine and 3.0 g (18 mmol) of *B*-triethylboroxin in 25 mL of anhydrous ether. An essentially quantitative yield of crude product, mp 113–115 °C, was obtained. An analytical sample, mp 115–116 °C, was obtained by recrystallization from diethyl ether or carbon tetrachloride. Anal. Calcd for $C_6H_{19}B_3N_2O_3$ (M_r 199.66): C, 36.09; H, 9.59; B, 16.24; N, 14.03; O, 24.03. Found: C, 35.93; H, 9.83; B, 16.20; N, 13.83.

NMR data: $\delta(^1H)$ 4.58* (4 H, s), 0.90 (9 H, t, $J = 7.5$), 0.59 (6 H, q, $J = 7.5$); $\delta(^{11}B)$ 23.9 (s, $h_{1/2} = 500$ Hz).

$(-BC_2H_5O-)_3 \cdot 2N_2H_4$ was obtained in similar fashion from 3 mL (94 mmol) of anhydrous hydrazine and 2.0 g (12 mmol) of *B*-triethylboroxin in 40 mL of ether. The crude colorless material was recrystallized from CCl_4 to give 2.7 g (98%) of purified product, mp 52–54 °C. If the material is kept under vacuum over P_4O_{10} at ambient temperature, it slowly but steadily loses hydrazine until it stabilizes at the stage of the 1:1 molar adduct. The latter is produced rapidly if the original product is held at 60–80 °C over P_4O_{10} and under vacuum.

NMR data: $\delta(^1H)$ 4.21* (4 H, s), 0.88 (9 H, t, $J = 7.5$), 0.55 (6 H, q, $J = 7.5$); $\delta(^{11}B)$ 22.5 (s, $h_{1/2} = 500$ Hz).

$(-BC_6H_5O-)_3 \cdot (CH_3)_2NNH_2$. A quantity, 1.0 g (17 mmol), of anhydrous *N,N*-dimethylhydrazine was slowly added to a stirred mixture of 5.0 g (16 mmol) of *B*-triphenylboroxin and 75 mL of benzene. The mixture was stirred at room temperature for 4 h, a small amount of remaining insoluble material was filtered off, and all volatile material was removed from the clear filtrate under reduced pressure. The resultant pasty residue was dissolved in a minimum amount of diethyl ether, the solution was filtered and volatiles were evaporated from the filtrate under reduced pressure at ambient temperature to leave 5.6 g (94%) of colorless crystals, mp 44–48 °C (after drying in vacuum over P_4O_{10} for 24 h). Anal. Calcd for $C_{20}H_{23}B_3N_2O_3$ (M_r 371.84): C, 64.60; H, 6.23; B, 8.72; N, 7.53; O, 12.91. Found: C, 63.29; H, 6.31; B, 8.43; N, 7.16.

NMR data: $\delta(^1H)$ 8.04 (6 H, m), 7.41 (9 H, m), 3.64* (2 H, s), 2.65 (6 H, s); $\delta(^{11}B)$ 20.5 (s, $h_{1/2} = 600$ Hz).

$(-\text{BC}_6\text{H}_5\text{O}-)_3 \cdot 2(\text{CH}_3)_2\text{NNH}_2$ was obtained in analogous fashion by addition of a large molar excess (3 mL = 40 mmol) of *N,N*-dimethylhydrazine to a stirred mixture of 2.3 g (7.4 mmol) of *B*-triphenylboroxin and 50 mL of ether. Most of the solid dissolved and the mixture was stirred at room temperature for 4 h, filtered, and volatiles were removed under reduced pressure. The remaining colorless material was recrystallized from ether and dried under vacuum at ambient temperature to give 2.8 g (87.5%) of product, mp 107-109 °C. Anal. Calcd for $\text{C}_{22}\text{H}_{31}\text{B}_3\text{N}_4\text{O}_3$ (M_r 431.95): C, 61.17; H, 7.23; B, 7.51; N, 12.97; O, 11.11. Found: C, 60.84; H, 7.08; B, 7.56; N, 12.88.

NMR data: $\delta(^1\text{H})$ 8.03 (6 H, m), 7.39 (9 H, m), 3.44* (4 H, s), 2.53 (12 H, s); $\delta(^{11}\text{B})$ 20.0 (s, $h_{1/2}$ = 600 Hz).

$(-\text{BC}_6\text{H}_5\text{O}-)_3 \cdot \text{CH}_3\text{HNNHCH}_3$ was prepared in analogous fashion as the preceding compound from a solution of 10 mmol of *N,N'*-dimethylhydrazine in 15 mL of ether and a mixture of 2.8 g (9 mmol) of *B*-triphenylboroxin and 50 mL of ether to give 3.05 g (91%) of colorless, moisture-sensitive material. The species loses hydrazine on heating under atmospheric pressure; a mp 102-105 °C decomp was observed in a sealed capillary.

NMR data: $\delta(^1\text{H})$ 8.04 (6 H, m), 7.40 (9 H, m), 4.2* (2 H, s), 2.61 (6 H, s); $\delta(^{11}\text{B})$ 22.0 (s, $h_{1/2}$ = 750 Hz).

$(-\text{BC}_6\text{H}_5\text{O}-)_3 \cdot \text{N}_2\text{H}_4$ was prepared in similar fashion from 0.3 mL (9.6 mmol) of hydrazine and a mixture of 2.8 g (9 mmol) of *B*-triphenylboroxin and 50 mL of ether. The crude product (3.25 g, mp 70-75 °C) was recrystallized from petroleum ether (bp 30-60 °C) to afford colorless crystals of purified material, mp 95-97 °C.

NMR data: $\delta(^1\text{H})$ 8.0 (6 H, m), 7.4 (9 H, m), 4.1* (4 H, s); $\delta(^{11}\text{B})$ 21.6 (s, $h_{1/2}$ = 1500 Hz).

$(-\text{BC}_6\text{H}_5\text{O}-)_3 \cdot 2\text{N}_2\text{H}_4$ was prepared in analogous fashion from 2.25 g (70 mmol) of hydrazine and 2.3 g (7.4 mmol) of *B*-triphenylboroxin in 50 mL of ether. The crude product (2.78 g of slightly yellow solid, mp 42-46 °C) was recrystallized from petroleum ether (bp 30-60 °C) to give an essentially quantitative yield of colorless crystals, mp 48-52 °C. The complex begins to lose hydrazine at about 60 °C under atmospheric pressure.

NMR data: $\delta(^1\text{H})$ 7.9 (6 H, m), 7.4 (9 H, m), 3.8* (8 H, s); $\delta(^{11}\text{B})$ 20.7 (s, $h_{1/2}$ = 600 Hz).

Results

When *B*-triethylboroxin, $(-\text{BC}_2\text{H}_5\text{O}-)_3$, and *N,N*-dimethylhydrazine, $(\text{CH}_3)_2\text{NNH}_2$, are mixed at room temperature (neat or in the presence of solvents such as toluene, benzene, or ether), interaction occurs in 1:1 molar ratio only (and independent of the employed stoichiometry of the reagents) to form the complex $(-\text{BC}_2\text{H}_5\text{O}-)_3 \cdot (\text{CH}_3)_2\text{NNH}_2$ as a clear distillable liquid.

At room temperature, the complex exhibits only one ^{11}B NMR signal at δ 23.8 (as compared to $\delta(^{11}\text{B})$ 33.7 (this work: 33.4) of the pure boroxin). The signal sharpens somewhat when the temperature is increased from ambient temperature ($h_{1/2} = 200$ Hz) to 50 °C ($h_{1/2} = 100$ Hz). On the other hand, when the temperature is lowered, a broadening of the ^{11}B NMR signal is observed and at -50 °C two signals at 31.4 and 6.9 ppm, respectively, are evident in approximately 2:1 area ratio. This illustrated in Fig. 1.

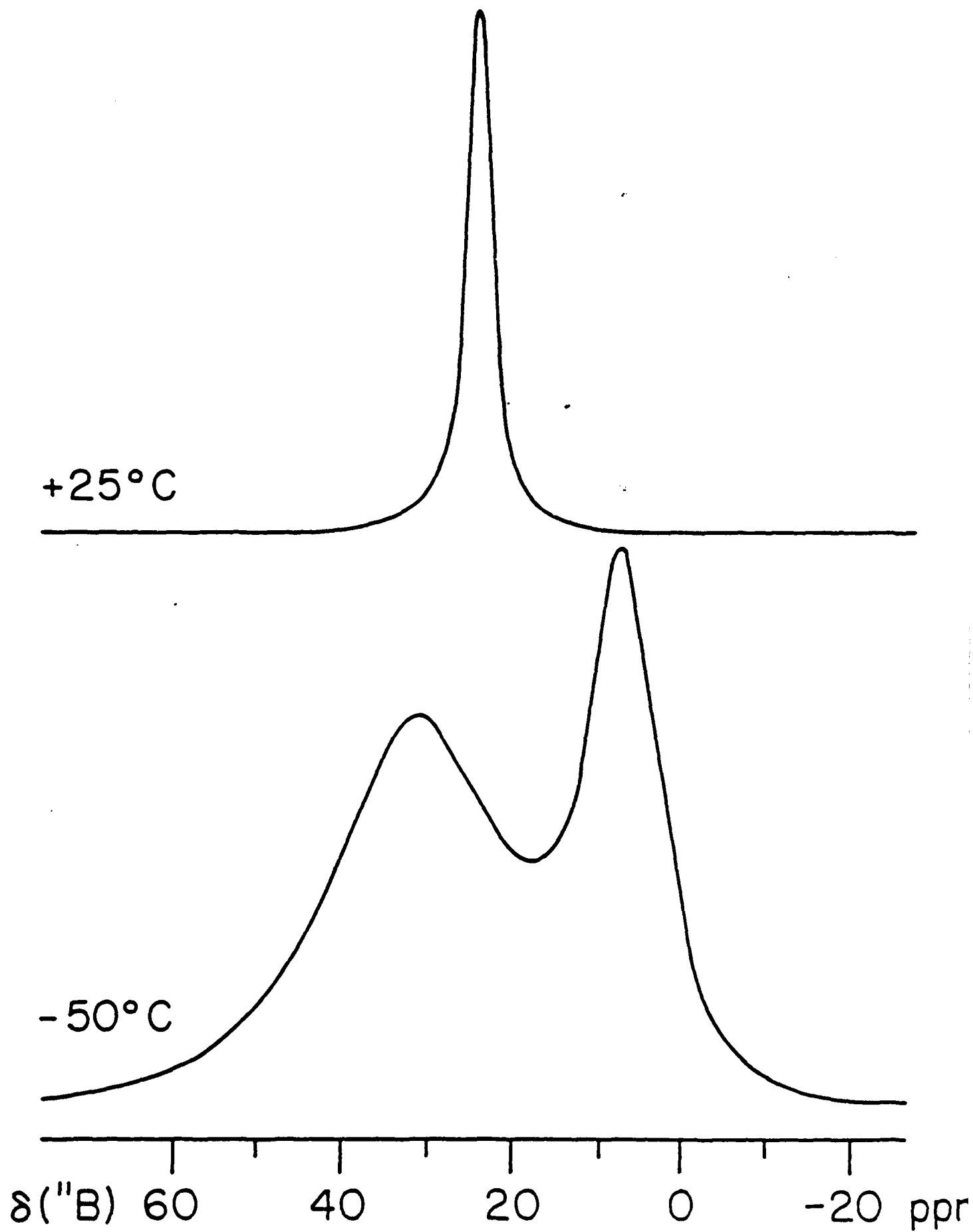
Figure 1

The cited observations suggest that the molecule is fluxional at room temperature and all three boron atoms of the boroxin ring are involved in the bonding as shown in A, above. However, at low temperatures, the nitrogen-to-boron coordination localizes at one boron atom of the boroxin ring (B, $\delta(^{11}\text{B})$ 6.9) and only one of the nitrogen atoms of the hydrazine seems to participate in the bonding.

The infrared spectrum of (neat) *N,N*-dimethylhydrazine exhibits N-H stretching as a strong and broad band near 3300 cm^{-1} with a shoulder near 3220 cm^{-1} . On the other hand, two sharp and distinct bands are observed near 3340 cm^{-1} (strong) and 3280 cm^{-1} (medium), respectively, in the infrared spectrum of (neat) $(-\text{BC}_2\text{H}_5\text{O}-)_3 \cdot (\text{CH}_3)_2\text{NNH}_2$. This observation suggests a lack of hydrogen bonding in the latter compound and makes the NH_2 moiety of the hydrazine likely to be the coordinating site.

Similarly, *B*-triethylboroxin interacts with hydrazine to form the complex $(-\text{BC}_2\text{H}_5\text{O}-)_3 \cdot \text{N}_2\text{H}_4$, and with *N,N'*-dimethylhydrazine to form $(-\text{BC}_2\text{H}_5\text{O}-)_3 \cdot \text{CH}_3\text{HNNHCH}_3$, two colorless solids. The latter complex is extremely hygroscopic. It can be purified by sublimation and does not decompose on melting. The room temperature ^{11}B NMR spectrum exhibits only one signal at 23.2 ppm. At 0 °C, the signal broadens, a shoulder appears near 31.2 ppm, and a small signal emerges near 0 ppm. At -50 °C, the latter has increased in intensity and

Figure 1. The ^{11}B NMR spectrum of $(-\text{BC}_2\text{H}_5\text{O}-)_3\cdot(\text{CH}_3)_2\text{NNH}_2$ at +25 and -50°C .



the overall signal is now extremely broad (ca. 2500 Hz) and unsymmetrical with maxima near 31, 23, and 0 ppm. As is the case with *N,N*-dimethylhydrazine, no species other than the 1:1 molar complex seems to be formed between *N,N'*-dimethylhydrazine and *B*-triethylboroxin.

The ^{11}B NMR signal of $(-\text{BC}_2\text{H}_5\text{O}-)_3\text{N}_2\text{H}_4$ also broadens on lowering of the temperature ($h_{1/2} = 1500$ Hz at 0 °C, ca. 4000 Hz at -40 °C) and, at -40 °C, there seems to be a signal emerging near 0 ppm. The compound does not decompose on melting; it readily sublimates under vacuum (at 30 °C) or even atmospheric pressure (at 150 °C).

The latter complex interacts with additional hydrazine to form solvates with variable quantities of excess hydrazine and a solid species of the composition $(-\text{BC}_2\text{H}_5\text{O}-)_3\cdot 2\text{N}_2\text{H}_4$ can be isolated. The solvation causes an upfield shift of the (N)H NMR signal of about 0.4 ppm. At room temperature, the ^{11}B NMR spectrum exhibits only one signal at 22.5 ppm. The signal broadens on lowering of the temperature and at -50 °C the broad ($h_{1/2}$ ca. 4000 Hz) signal is unsymmetric and shows two maxima at 32.0 and 2.2 ppm, respectively, suggesting two overlapping signals in an (estimated) area ratio of 1:2. This observation may be interpreted that one nitrogen atom each of the two hydrazine molecules localizes at a different boron atom of the boroxin ring.

The room temperature NMR data may also be interpreted to reflect an exchange of coordinated and free hydrazine. However, the moisture-sensitive $(-\text{BC}_2\text{H}_5\text{O}-)_3\cdot 2\text{N}_2\text{H}_4$ is thermally unstable and loses hydrazine readily at 60-80 °C and under vacuum, slowly on prolonged storage under vacuum at ambient temperature, ultimately forming the 1:1 molar complex. This observation lends credence to the suggested concept of solvation.

B-Triphenylboroxin reacts with hydrazines in a fashion analogous to that of *B*-triethylboroxin. The 1:1 molar complex with $(\text{CH}_3)_2\text{NNH}_2$ does not appear to be moisture-sensitive (the ^1H NMR spectrum of a material exposed to laboratory atmosphere for 24 h was identical with that of a freshly prepared product) but the adduct is thermally fairly unstable. Decomposition to the individual components was observed to occur near 100 °C under vacuum. The complex $(-\text{BC}_6\text{H}_5\text{O}-)_3\cdot 2(\text{CH}_3)_2\text{NNH}_2$ was also isolated; it is thermally quite unstable and, after melting, begins to decompose into the individual components. The room temperature ^{11}B NMR data for both the 1:1 and the 1:2 complex are essentially identical.

$(-\text{BC}_6\text{H}_5\text{O}-)_3\cdot \text{CH}_3\text{HNNHCH}_3$ is extremely hygroscopic and thermally not very stable. On heating under atmospheric pressure it loses hydrazine even before melting. No other adduct composition between the two agents was observed.

B-Triphenylboroxin and hydrazine interact in both 1:1 and 1:2 molar ratio. Of these adducts, the 1:1 molar complex does not readily decompose on melting but decomposes to the components on heating to 90-100 °C under vacuum. The 1:2 species loses hydrazine just above its melting point (48-52 °C) and under atmospheric pressure. Thereafter the thermal behavior is analogous to that of the 1:1 complex.

Discussion

Hydrazines interact readily with *B*-triorganylboroxins to form 1:1 molar complexes. The room temperature ^{11}B NMR data show that these complexes are fluxional and all three boron atoms of the boroxin are involved in the bonding. At low temperatures, however, the N-to-B coordination is localized at only one boron atom rendering it to be sp^3 hybridized, whereas the other two boron atoms are in sp^2 environment. These observations also imply that the hydrazines function exclusively in monodentate fashion when interacting with boroxins. Otherwise, the observed ratio of the ^{11}B NMR signals for three-coordinate versus four-coordinate boron should be in the reverse order to show bidentate intramolecular coordination, or the hydrazines should form 1:2 molar complexes with the boroxins, which is not the case. On the other hand, it is possible that more than one hydrazine molecule coordinates to a single boroxin ring. However, such additional interaction is very weak and may be viewed as solvation rather than coordination. This interpretation is supported by the ready loss of excess (as compared to a 1:1 molar ratio) of the hydrazine. There is little if any difference in the ambient temperature ^{11}B NMR spectra of the 1:1 complexes and the solvated species.

It is worth noting that such solvated complexes were observed only in cases where the hydrazine contained at least one NH_2 group. This suggests that the NH_2 group of *N,N*-dimethylhydrazine is the more likely donor site in this 1:1 complexes. Coordination of the sterically least hindered donor site is also in consonance with some infrared data. Furthermore, a steric effect is also suggested by the different thermal stabilities of the various species, i.e., with increasing steric crowding (either at boron or at nitrogen) the thermal stabilities of the adducts decrease. However, the different thermal stabilities are not reflected by the room temperature ^{11}B NMR data, since all compounds exhibit a (single) signal in the 20-24 ppm range. The 70 eV mass spectra of all of these complexes exhibit only the fragmentation patterns of the individual components. Very weak parent ion clusters of the 1:1 molar complexes could be observed in some cases in the 14 eV spectra.

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Footnote and References

† On leave from Jadavpur University, Calcutta, India.

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